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Conrad W. Ingram

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223 James P. Brawley Drive SW
Atlanta, GA 30314 -4358

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14. ABSTRACT
Clark Atlanta University (CAU) acquired a Panalytic Empyrean X-Ray diffractometer with wide angle (WAXS) and small angle scattering (SAXS) 1D and 2D capabilities to support its chemistry, physics, and materials science research and education activities. This XRD has become a primary research instrument that is currently utilized in conjunction with other instrumentation at CAU to support research activities in the following areas: (1) Polymer-inorganic nanocomposites; (2) Materials and Manufacturing Exploration in Support of Air Force Systems and Applications: Multiscale modeling of advanced organic matrix composite materials systems; (3) Graphene oxide

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Report Title

Final Report: Acquisition of an X-Ray Diffractometer with WAXS and SAXS for Materials Research

ABSTRACT

Clark Atlanta University (CAU) acquired a Panalytic Empyrean X-Ray diffractometer with wide angle (WAXS) and small angle scattering (SAXS) 1D and 2D capabilities to support its chemistry, physics, and materials science research and education activities. This XRD has become a primary research instrument that is currently utilized in conjunction with other instrumentation at CAU to support research activities in the following areas: (1) Polymer-inorganic nanocomposites; (2) Materials and Manufacturing Exploration in Support of Air Force Systems and Applications: Multiscale modeling of advanced organic matrix composite materials systems; (3) Graphene oxide nanoribbons (GONRs) based heterophase elastomeric conductive composites: Preparation, characterization, modeling and property evaluation; (4) Polymer-graphene nanocomposites; (5) Polymer/nanocellulose nanocomposites; and (6) Development of organic-inorganic hybrid metal organic framework (MOF) structures for applications in radiation element detection and as heterogeneous catalysis for degradation of chemical warfare agents. The instrument will be utilized to investigate molecular structure, strain in crystallites, crystallinity, phase purity, thermal stability, phase changes, particle size and pore size distribution and dispersion, of nanophases by taking advantage of its WAXS and SAXS features. The WAXS feature is being utilized for high-quality phase identification and quantification, determination of crystallite size, preferred orientation and strain of individual crystallites present in polycrystalline and ordered (nano) phases in powders and thin films. The incorporation of the SAXS capabilities allows for the investigation of particle and pore size distribution, dispersion, specific surface area, degree of exfoliation and delamination of nanophases.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

none

Patents Awarded

none

Awards

none

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Stephan Mathis II	0.00	
Saki Golafale	0.00	
Lionel Cross	0.00	
William Simmons	0.00	
Charity Burgos	0.00	
Jamila Marshall	0.00	
John Melnyczuk	0.00	
Frank Ikponmwen	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**8**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Huayang Li	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Dr. James Reed	0.00	
Dr. Conrad W. Ingram	0.00	
Dr. Eric Mintz	0.00	
Dr. Xia Bu	0.00	
Dr. Ishrat Khan	0.00	
Dr. Xiao-Qian Wang	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**6**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Kierra Whittle	0.00	Chemistry
Kymberli Hill	0.00	Chemistry
Jontae Edgecombe	0.00	Chemistry
Vasthi Jean Mitchel	0.00	
October R. Martinez	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**5**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 2.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 2.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME
Charity Burgos -expected graduation
Jamila Marshall-expected date of grad
Total Number: **2**

Names of personnel receiving PHDs

NAME
Stephan Mathis II-Expected graduatio
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
Biswajit Sannigrahi	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The Panalytical Empyrean X-ray Diffractometer was installed at CAU and commissioned in November 2014. Onsite training by the vendor was conducted in February 2015. Most of research activities involving the use of the instrument is within the first months since the instrument was installed, and therefore with infancy.

All personnel identified in this report are actively utilizing the instrument for research in the following topical areas: (1) Polymer-inorganic nanocomposites; (2) Materials and Manufacturing Exploration in Support of Air Force Systems and Applications: Multiscale modeling of advanced organic matrix composite materials systems; (3) Graphene oxide nanoribbons (GONRs) based heterophase elastomeric conductive composites: Preparation, characterization, modeling and property evaluation; (4) Polymer-graphene nanocomposites; (5) Polymer/nanocellulose nanocomposites; and (6) Development of organic-inorganic hybrid metal organic framework (MOF) structures for applications in radiation element detection and as heterogeneous catalysis for degradation of chemical warfare agents. The instrument is utilized to investigate molecular structure, strain in crystallites, crystallinity, phase purity, thermal stability, phase changes, particle size and pore size distribution and dispersion, of nanophases by taking advantage of its WAXS and SAXS features. The WAXS feature is utilized for high-quality phase identification and quantification, determination of crystallite size, preferred orientation and strain of individual crystallites present in polycrystalline and ordered (nano) phases in powders and thin films. The incorporation of the SAXS capabilities allows for the investigation of particle and pore size distribution, dispersion, specific surface area, degree of exfoliation and delamination of nanophases.

Technology Transfer

None yet

Scientific Progress

1. Introduction

The Panalytical Empyrean Series II X-ray Diffractometer was installed at CAU and commissioned in November, 2014. Onsite training by the vendor was conducted on the 4th and 5th of February, 2015. Several potential CAU instrument users, including eight graduate and five undergraduate students, three faculty members, one postdoc, and one staff scientist were train in various aspects of its basic operation and use. Acquiring this instrument is critical towards augmenting CAU's capabilities to perform cutting edge research in areas of vital importance to the mission and research needs of the Department of Defense (DoD) and its research offices. the Within the last four months since the instrument installation, all personnel identified in this report have been actively utilizing the instrument for research and training and have made significant progress in the following topical areas that were detailed in the original proposal:

a. Development of organic-inorganic hybrid metal organic framework (MOF) structures for applications (i) in radiation element detection, (ii) as adsorbents for organic and heavy metal contaminants, and, (iii) heterogeneous catalysis for degradation of chemical warfare agents
b. Polymer-inorganic nanocomposites
c. Polymer-graphene nanocomposites
d. Polymer/nanocellulose nanocomposites
e. Iron oxide-nanoparticles- single wall carbon nanotube composite for electronic and magnetic applications

The instrument is utilized to investigate molecular structure, strain in crystallites, crystallinity, phase purity, thermal stability, phase changes, particle size and pore size distribution and dispersion of nanophases by taking advantage of its wide angle z-ray scatter (WAXS) and small angle X-ray scatter (SAXS) features. The WAXS feature is utilized for high-quality phase identification and quantification, determination of crystallite size, preferred orientation and strain of individual crystallites present in polycrystalline and ordered (nano) phases in powders and thin films. The incorporation of the SAXS capabilities allows for the investigation of particle and pore size distribution, dispersion, specific surface area, degree of exfoliation and delamination of

nanophases. A summary on the use of the instrument to advance research in each topical area is given below project.

2. Research Progress

a) Development of organic-inorganic hybrid metal organic framework (MOF) structures for applications i) in radiation element detection, ii) as adsorbents for organic contaminants, and, iii)heterogeneous catalysis for degradation of chemical warfare agents

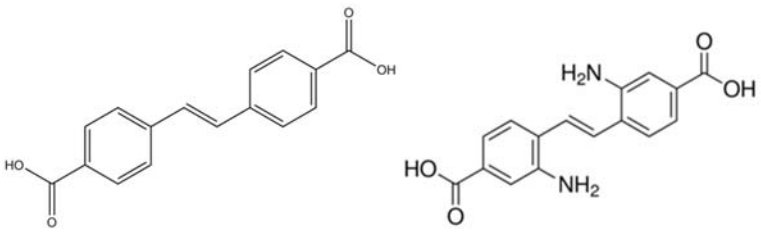
Advancement in radiation detection technology is needed for more reliable, more efficient and less costly detection of radiation from fissile materials. The Office of Naval Research, division of Materials and Chemistry has keen interest in basic and applied research to generate new and improved materials with emphases on affordability, performance, survivability, warfighter protection, chemical, biological and radiological element detection, and life extension, consistent with the principal focus areas of the Naval S&T Strategic Plan and naval capabilities. Design of advanced devices and systems critically depends on the development of improved materials.

(i) Metal organic framework (MOFs) for detection of radiation

MOFs are a special class of porous coordination polymeric materials that are of great significance and rapidly growing interest due to their promising applications in many areas, including luminescence, optical and chemical sensing and molecular recognition, adsorption, ion exchange, gas storage, catalysis, and magnetism. Their assembly involves strong coordination of metal ions or metal clusters and organic linkers to produce extended 0D, 1D, 2D or 3D structures, with unprecedented high surface areas (up to 5900 m^2/g), large and permanent porosities (up to 2 cm^3/g) in many cases, and a wide range of pore dimensions and topologies. Their chemical sensing and detection capabilities are based on solvochromatic shifts, alteration of the electronic structure via changes in the coordination sphere, and fluorescence quenching from interactions (e.g. π-π interaction, hydrogen bonding, and electrostatic interactions.) of the adsorbed species with the ligand or absorption of the fluorescent signal by the species.

We have recently synthesized several 3-D MOFs, containing large pores. For example, we synthesized a new 3D-luminescent MOF containing the photo emissive ligand linker, 4,4'-trans-

stilbene dicarboxylic acid, **1,** and a lanthanide element. The structure contains extremely large pores of dimensions 30.7 Å x 14.1 Å and with solvent accessible volume occupying 60-70% percent of the structure (Figure 1). The structure shows strong red shifted ligand-based luminescence emission on excitation at λ_{ex} of 341 nm (Figure 2). We anticipate that its open structure will be capable of adsorbing and concentrating the targeted analytes. The luminescence behavior of this structure on exposure to 2-chloroethyl ethylsulfide (CEES) and dimethyl methylphosphonate (DMMP) as chemical warfare agent simulants will be investigated. In addition, we will investigate performance of MOFS that is synthesized using the diamino-substituted analogue, 2,3′-diamino-4,4′-stilbenedicarboxylic acid, **2**. This ligand is known as a sensitizer for applications in dye-sensitized solar cells, and the presence of the amino groups could potentially enhance its luminescence characteristics.



1 **2**

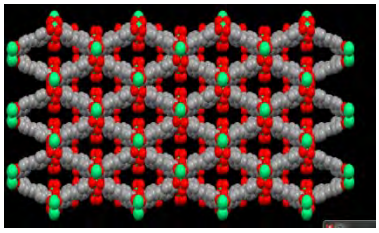


Figure 1: Large pore 3D-stilbene based lanthanide MOF

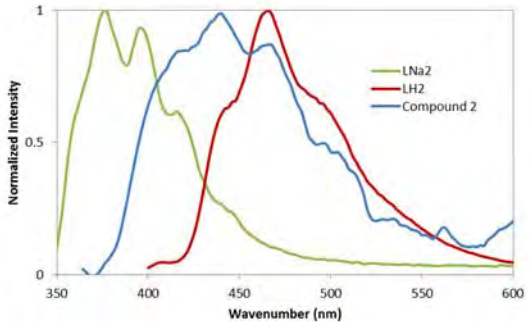
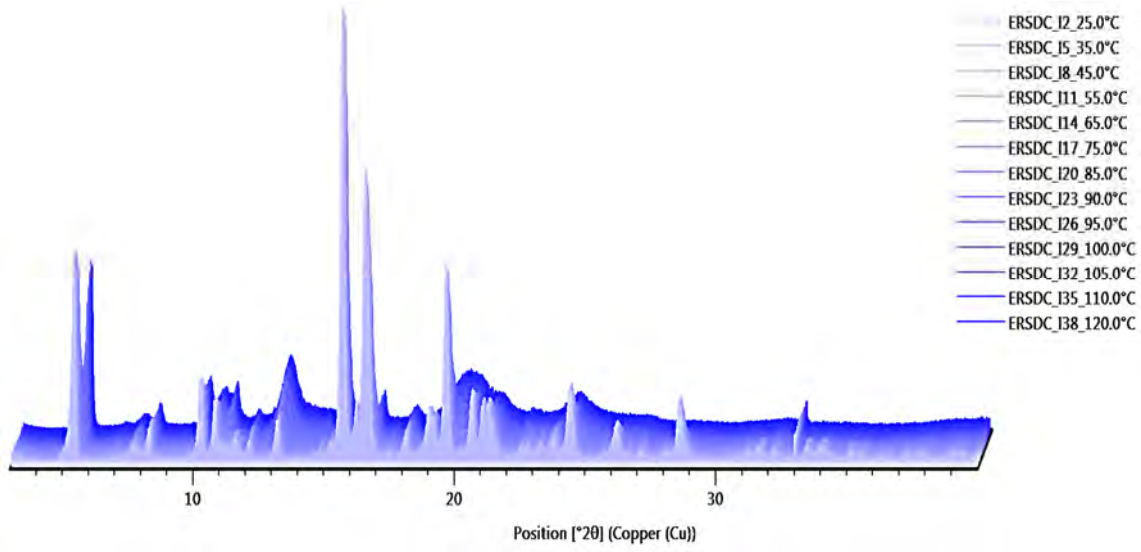


Figure 2: Emission spectra of stilbene lanthanide MOF (Compound 2) and pure stilbene dicarboxylic acid, LH_2.

The large pore SDC-based MOF was further investigated for phase changes under increasing temperature conditions, using the non-ambient feature of the Empyrean Series 2 XRD system (Figure 3). Phase change was observed around 85ºC. The identity of the new phase is under further investigation.



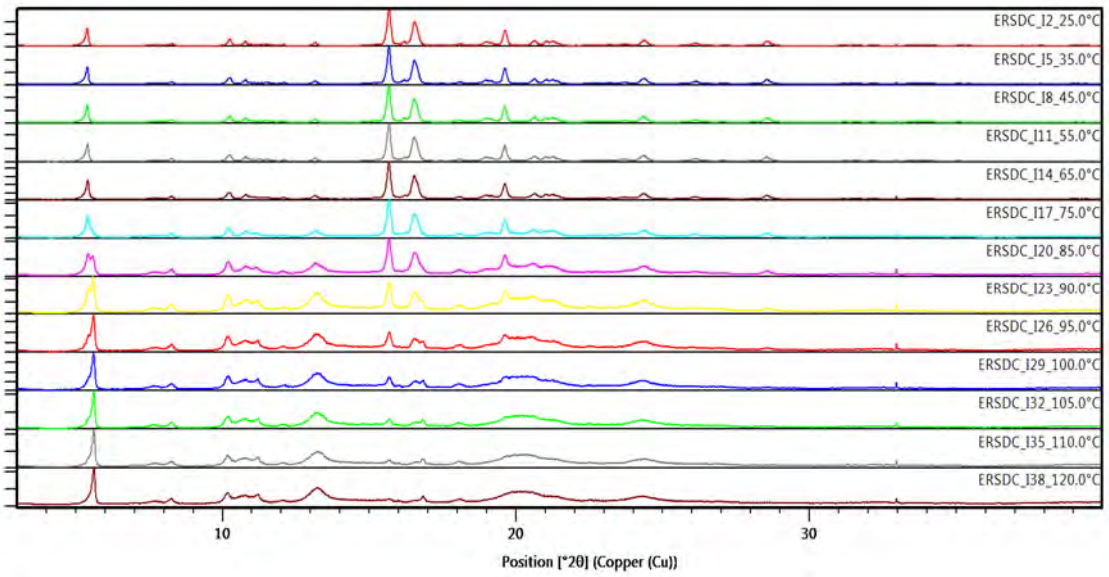


Figure 3. PXRD profiles of novel SDC-based large pore fluorescent metal organic framework structure 4, with temperature variation: (top) 3D XRPD patterns from 25°C to 120°,(bottom) stacked conformation of diffraction patterns from 25°C to 120°C.

(ii) MOFs as adsorbents for organics and heavy metals: MOFs are well known for their various applications in the field of adsorption and separation. MOF-235 is an iron-terephthalate metal-organic framework composed of non-toxic Fe_3O clusters and easily synthesized at low temperatures. In MOF-235, the iron atoms have a valence of 3, yielding an overall cationic framework with a charge of +1. This charge is balanced by $FeCl_4^{-1}$ counterions that are located in the hexagonal pores of the structure. We have synthesized MOF-235 and we are investigating its properties for the adsorption of organics from water. Successful synthesis of the structure was confirmed using PXRD (Figure 4) among other complementary techniques.

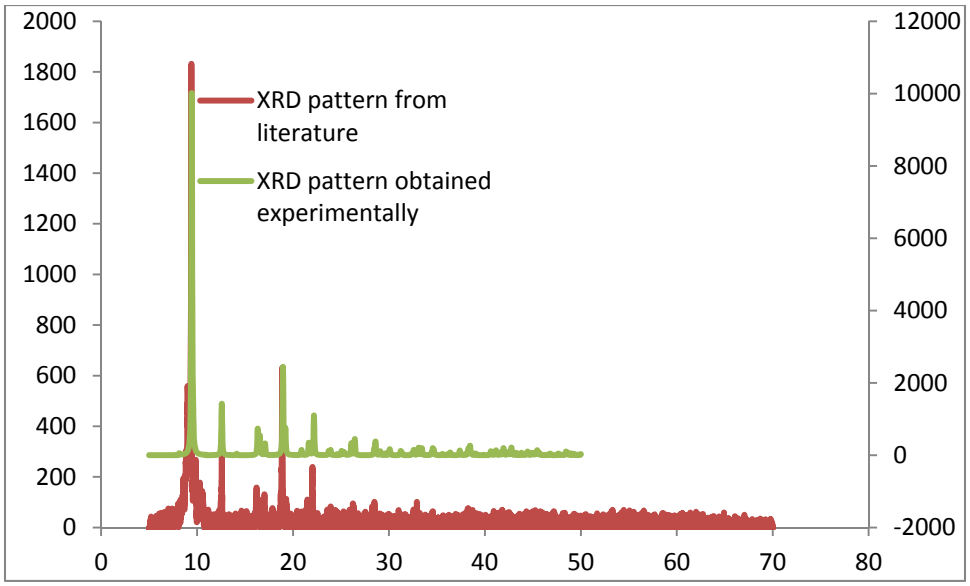
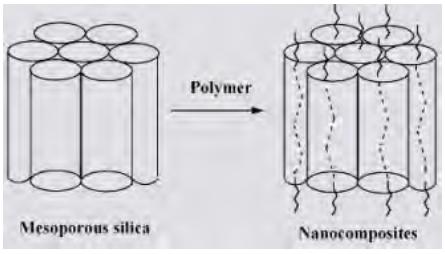


Figure 4. XRD was performed to check the structure. The diffraction profile displays peaks that correlate with the XRD image from literature, thus indicating that the material was successfully synthesized.

(iii) Mesoporous silica as adsorbents for organics and heavy metals: Mesoporous silicas containing uniform pore sizes and rigid pore structures are a particularly interesting class of materials as potential adsorbents. In particular, mesoporous silica, SBA-15 is a highly thermally stable material contain



hexagonal array of uniform nanotubes with surface area in the range of 1000 m^2/g and pore diameters 1.5-30 nm. Its pore size and surface chemistries can be extended using relatively inexpensive block copolymers, e.g. pluronic 123 ($EO_5PO_{70}EO_5$). Functionalization of the internal pores with organic species can render the porous material more amenable to interactions with the adsorbates. We are therefore investigating the use of organofunctionalized ordered mesoporous silicates as adsorbents for organics and heavy metals: materials containing varying inorganic reactants. The functionalization agents being investigated are trimethylsilyl propyl ethylenediamine (TMSPED), diethylenetriamine pentaacetic acid anhydride (DTPA) and ethylenediamine tetraacetic acid (EDTA) We have found that the inorganic and the organic containing nanoporous silicates are stable up to 500^0C. We are utilizing small angle X-ray

scattering (SAXS) low angle XRD to characterize the synthesis of the ordered mesoporous organosilicates.

The "as synthesized" and functionalized SBA-15 were both characterized to ascertain their physiochemical properties. Half angle XRD patterns which exhibited four peaks with three well resolved peaks with d = 8.2, 5.1, 4.5 nm was indexed as the (100), (110) and (200) reflections associated with typical two dimensional hexagonal symmetry (p6mm) (Figure 5). Similarly, XRD patterns were determined for TMSPED-DTPA-SBA-15 and compared to its parent, SBA-15. The result indicated that the hexagonal symmetry of SBA-15 was preserved (Figure 5). TMSPED-DTPA-SBA-15 showed d-spacing at 9.02 nm and a unit cell lattice parameter, a_o, as 10.4 nm which are typical of that reported for EDTA-SBA-15 and NH_3-SBA-

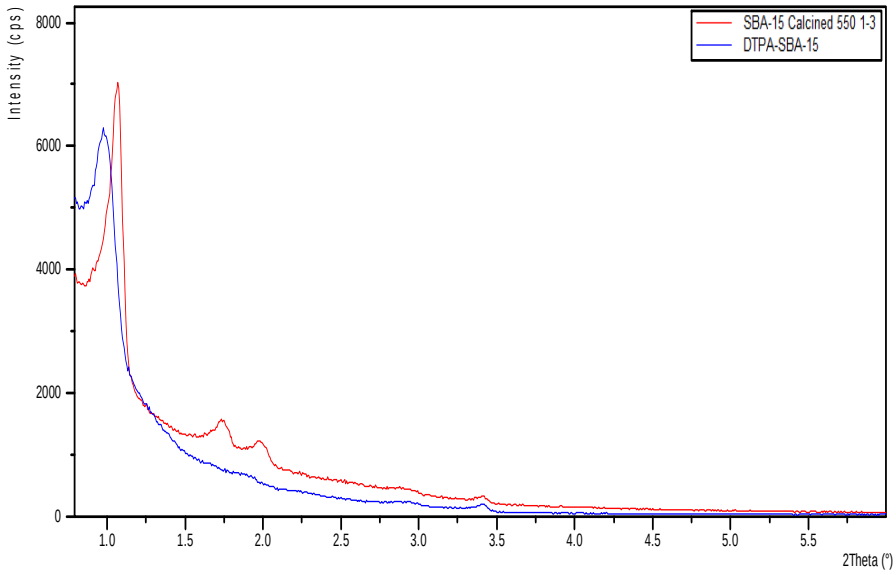


Figure 5. Showing Mesoporous SBA-15 silica absorbent before (blue) and after (red) functionalization with amino organosilane organic substituent.

(b) Polymer–inorganic nanocomposite for heterogeneous catalysis:

Embedding the photocatalytic mix phase TiO_2 into a polymer matrix can generate polymer–inorganic nanocomposite that is useful for the photo degradation of chemical warfare agents.

Powdered 2D XRD shows that we can embed TiO_2 into a polymer reaction with no physical changes to the TiO_2 (Figure xxx). The image shown in (A) is the result from the 2D scan and

indicates that there are two distinct phases. The 1D XRD profile of the sample shows peaks corresponding to only two phases, namely, anatase (blue) and rutile (green). Quantitative analysis shows an 88% to 12% anatase to rutile ratio and matches the initial composition of 80% to 12% reported by the supplier.

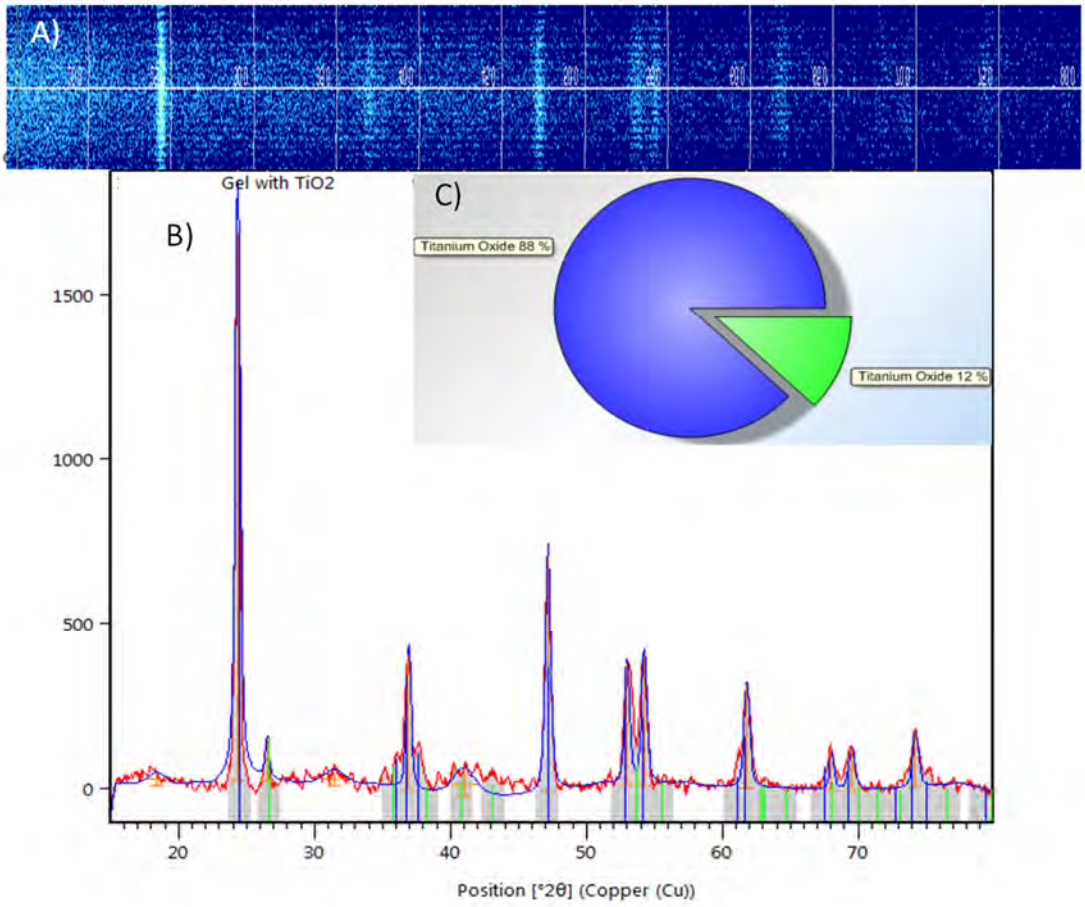


Figure 6. 2D XRD to show that we can embed mix phase TiO_2 into a polymer matrix with no physical changes to the TiO_2 somposition.

c. Polymer-graphene nanocomposites

We are examining the incorporation and de-stacking of graphite in phenylethynyl terminated imide resins. Resins currently under study include PETI 298 and 330 and RTM 370. PETI 298 is formulated from symmetrical 2,3,3′,4′-biphenyltetracarboxylic dianhydride (s-BPDA), 1,3,-bis(3-aminophenoxy)benzene (1,3,3-APB), 3,4′-oxydianliline (3,4′-ODA) and end-capped with PEPA. PETI 330 is formulated with asymmetrical 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA) along with mixtures of 1,3-bis(4-

aminophenoxy)benzene (1,3,4-APB) and m-phenylendiamine (m–PDA), and a PEPA end-cap. RTM 370 is formulated with a-BPDA, 3,4'-oxydianinline (3,4'-ODA) and terminated with the PEPA end-cap components shown in Figure 7. These PIT resins have been shown to be thermally stable at 280 ^{o}C for at least 2 hr, and cure at temperatures above 340 °C over several hr. We have found that high torque melt mixing of graphites in PEIT 298 and PEIT 330 leads to dispersion de-stacking of the graphite leading to nanocomposites while the RTM 370 alone does not. All three resins contain electron withdrawing groups, aromatic imides. However, PETI 298 and PETI 330 contain an electron rich aromatic ring with two π donor oxygen atoms in 1,3,3-APB and 1,3,4-APB, respectively which is absent in RTM 370. We believe that the combination of the electron rich and electron withdrawing ring in the polymer backbone leads to a synergistic charge transfer interaction with graphene which supports the dispersion and delamination. While the PTI resins that we received are powders that have proved to be amorphous, with the high sensitivity of the Panalytical Empyrean XRD we have now been able to observe that upon melt mixing at 170 ^{o}C (no reaction) and cooling the PETI 298 peaks in the XRD suggest that ordered structures have developed that may include charge transfer complexes in the neat resin as shown in the Figure 8.

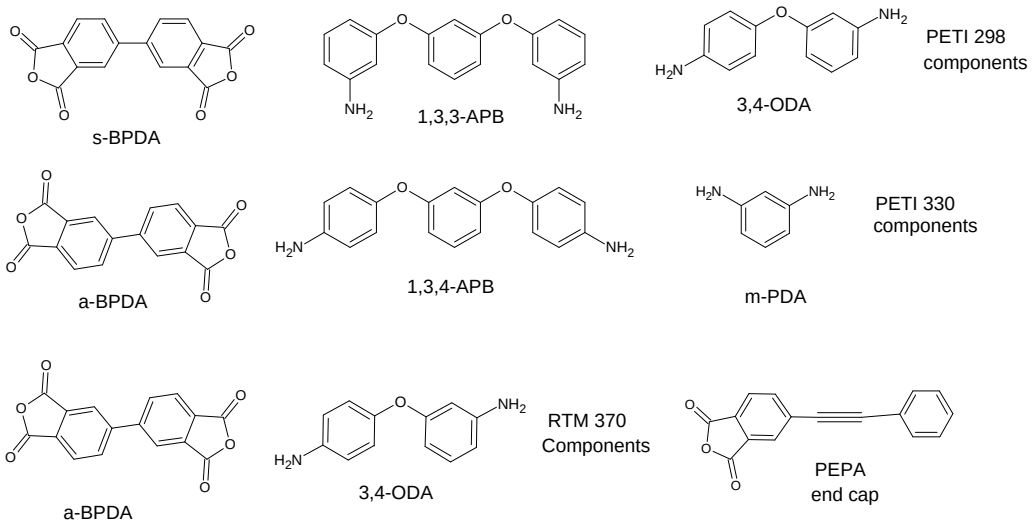


Figure 7. Components used in the preparation of PETI 298, PETI 330, and RTM 370.

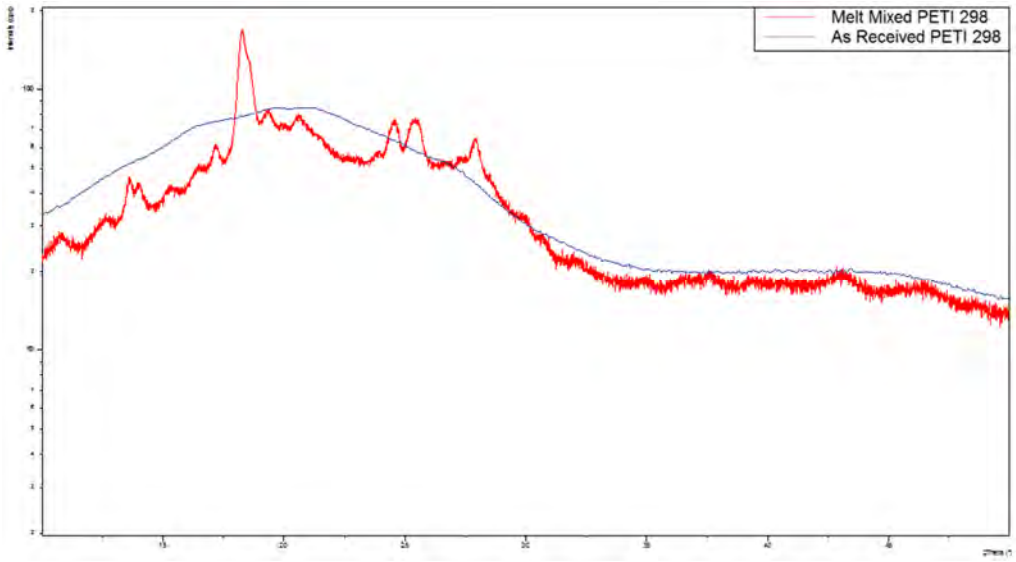


Figure 8. X-Ray Diffraction pattern of as- received PETI-298 and Melt Mixed PETI-298.

d. Polymer/nanocellulose nanocomposites

Natural cellulose based materials (wood, hemp, cotton, linen, paper, etc.) have been used by our society for thousands of years and have proven to be nontoxic and biocompatible. Cellulose nanocrystals (CNCs) are the basic building blocks for these natural cellulose based materials. CNCs are now being extracted from wood pulp derived from trees, by a variety of processes at the lab and pilot scale. CNCs can also be derived from grasses and bio-waste. CNCs have been found to exhibit greater elastic modulus along the chain than Kevlar and its mechanical properties are within the range of other nano-reinforcement materials. CNCs have a high aspect ratio, low density (1.6 g/mL), low coefficient of thermal expansion (CTE; ~0.1 x 10^{-6}/K), and reactive surface –OH groups that can facilitate grafting chemical species to achieve different surface properties, thus making them excellent candidates for use as fillers in bio-based biodegradable composite materials. These CNCs are environmentally safe sustainable, biodegradable, carbon neutral, and have low environmental, health and safety risks.

Figure 9 below shows that the sulfuric acid process used to isolate CNCs from dissolving pulp disrupts that crystalline phase and generates additional phases. We are examining other CNCs

produced under milder reaction conditions and correlating the crystal quality with thermal stability and developing predictive models for composite processing conditions.

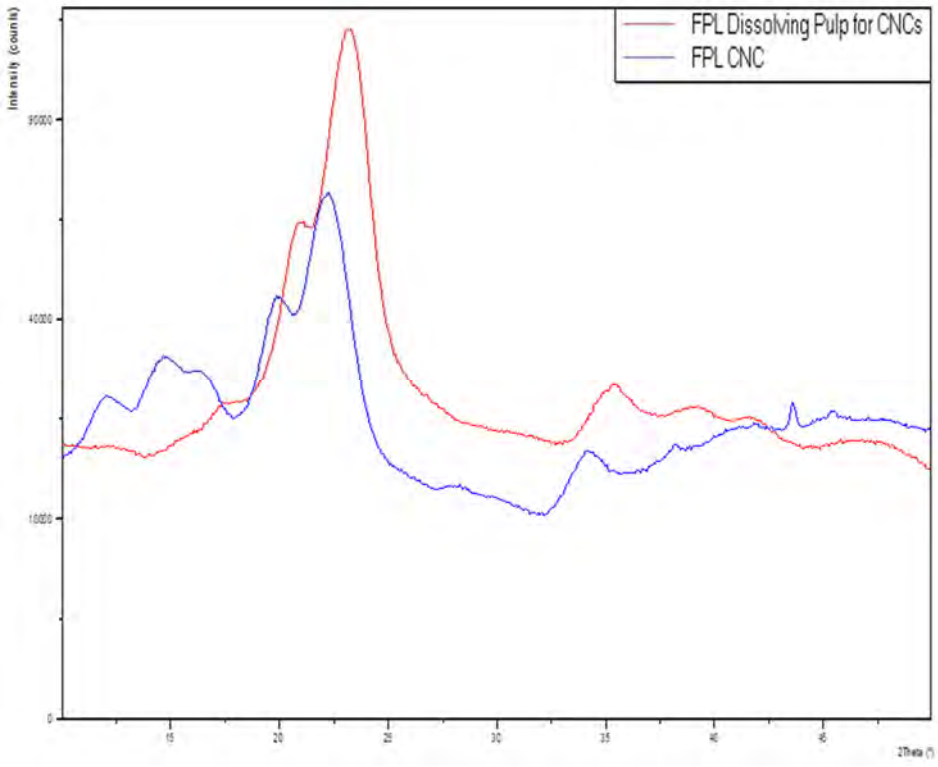


Figure 9. XRD of dissolving pulp and CNCs derived from it.

(e) Iron oxide-nanoparticles- single wall carbon nanotube composite for electronic and magnetic applications

Iron oxide nanoparticle-single wall carbon nanotube (SWCNT) composites are important materials for application in magnetic storage materials and high efficiency batteries. Nanohybrid of SWCNT and iron oxide nanoparticles of varying morphologies were prepared and were shown to demonstrate different electronic and magnetic properties compared to pure SWCNT or the iron oxide nanoparticles. The PXRD profiles of the hybrids show the characteristic XRD signals of carbon nanotube in 20-40 degrees and 45 degrees 2θ regions and were assigned to the graphite lattice. However, when iron oxide nanoparticles are attached onto carbon nanotube surface, the

graphite lattice signals show significant changes in 10-30 degree 2θ region (Figure 10). The change suggested significant electronic interaction between the graphite lattice and the nanoparticles.

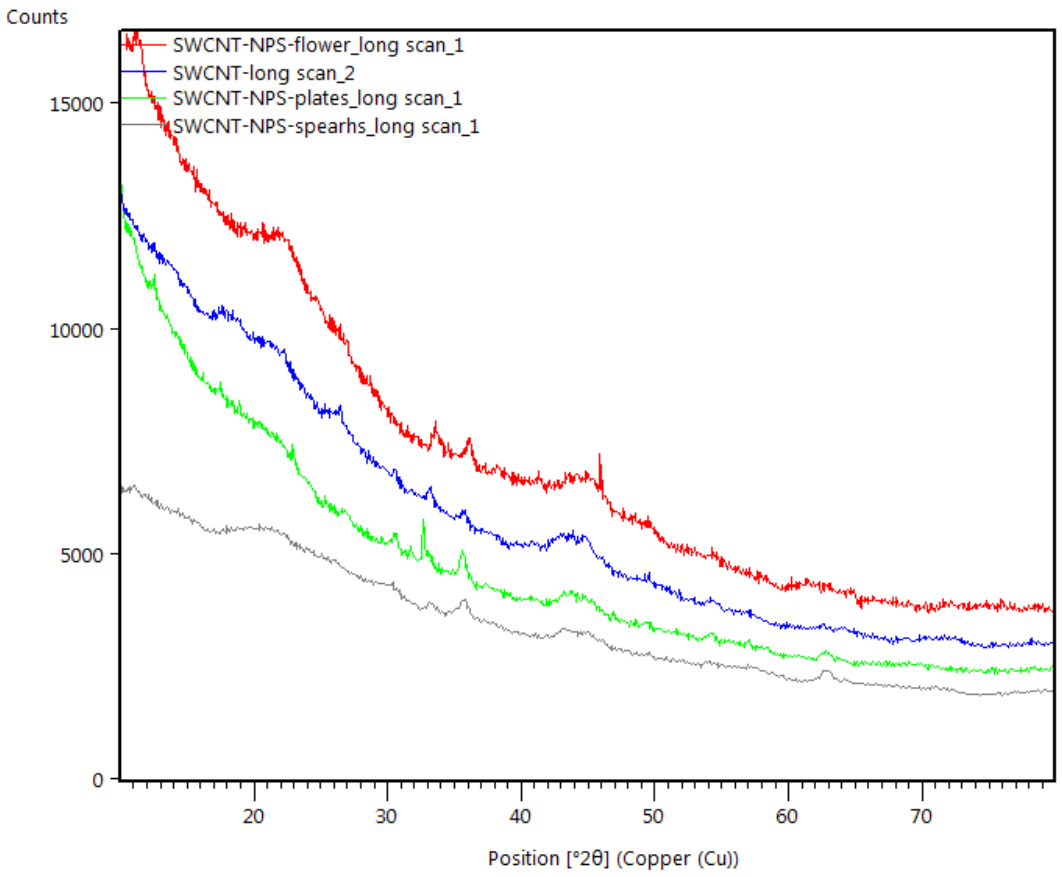


Figure 10. XRD profiles of hipocoSWCNT-shaped iron oxide nanoparticles nanocomposites